(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
22 February 2001 (22.02.2001)

PCT

(10) International Publication Number
WO 01/12876 A1

(51) International Patent Classification⁷: C23C 22/05, 22/00, C09D 5/00, 183/00

(21) International Application Number: PCT/US00/22363

(22) International Filing Date: 14 August 2000 (14.08.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
11230094 16 August 1999 (16.08.1999) JP

(71) Applicant (for all designated States except US): HENKEL CORPORATION [US/US]; Suite 200, 2500 Renaissance Boulevard, Gulph Mills, PA 19406 (US).

(72) Inventors; and
(75) Inventors/Applicants (for US only): KINOSHITA, Yasuhiro [JP/JP]; 2566, Shinomiya, Hiratsuka-shi, Kanagawa Pref 254-0014 (JP). MIZUNO, Kensuke [---/JP]; 23-5-204, Toyohara-cho, Hiratsuka-shi, Kanagawa Pref 254-0051 (JP). KAWAKAMI, Katsuyuki [---/JP]; 2393-11, Oyama-machi, Machida-shi, Tokyo 194-0212 (JP).

(74) Agent: HARPER, Stephen, D.; Henkel Corporation, Suite 200, 2500 Renaissance Boulevard, Gulph Mills, PA 19406 (US).

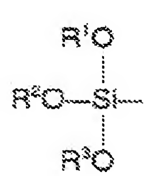
(81) Designated States (national): CA, CN, CZ, KR, MX, PL, TR, US.

(84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published:
— *With international search report.*
— *Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS AND COMPOSITION FOR TREATING METALS



(I)

(57) Abstract: An aqueous liquid surface treatment composition that comprises (i) molecules each of which contains at least two moieties that conform to general formula (I) wherein each of R^1, R^2, and R^3 is independently selected from the group consisting of hydrogen atoms and alkyl moieties containing from 1 to 4 carbon atoms, all of these molecules together having a quotient of average molecular weight to the average number per molecules of moieties conforming to formula (I) that is within a range from 100 to 30,000, and (ii) one or more substances selected from the group consisting of organic acids, phosphoric acid, hydrofluoric acid, tetrafluoroboric acid, hexafluorosilicic acid, hexafluorotitanic acid, hexafluorozirconic acid, hexafluorohafnic acid, and ammonium salts of organic acids, phosphoric acid, hydrofluoric acid, tetrafluoroboric acid, hexafluorosilicic acid, hexafluorotitanic acid, hexafluorozirconic acid, and hexafluorohafnic acid produces a highly corrosion-resistant, strongly paint-adherent film on metal surfaces without using a chromium containing composition.

WO 01/12876 A1

Description

PROCESS AND COMPOSITION FOR TREATING METALS

FIELD AND BACKGROUND OF THE INVENTION

This invention relates to a surface treatment agent that can form a highly corrosion-resistant, strongly paint-adherent film on the surface of a metal, e.g., steel sheet, zinciferous-plated steel sheet, and aluminum sheet. The invention also relates to a process for treating metal surfaces using this surface treatment agent.

Zinciferous-plated steel sheet is used in a variety of fields, for example, in automotive applications, for household electrical appliances, and as a building material. Since zinciferous-plated steel sheet corrodes upon exposure to the atmosphere with the production of a corrosion product known as white rust, it has heretofore typically been treated with a treatment composition containing an aqueous chromic acid solution in order to improve its corrosion resistance. This treatment, known as a chromate treatment, forms a coating layer that contains hexavalent chromium and trivalent chromium on the surface of zinciferous-plated steel sheet.

Unfortunately, since the aqueous solutions used in chromate treatment contain human-toxic hexavalent chromium, waste water treatment must in most jurisdictions comply with specific and detailed legal regulations. This has resulted, in association with the recent heightening of concern with global environmental preservation, in a strengthening of the desire to reduce the use of human-toxic compounds to the greatest extent possible.

Within the field of non-chromate surface treatment processes, treatment with tannic acid-containing surface treatment agents is well known. It is thought that the protective coating formed by the reaction of tannic acid and the metal during treatment with an aqueous tannic acid solution improves the resistance to corrosion by inhibiting the infiltration of corrosive substances. This coating, however, is essentially unable to meet the corrosion resistance and paint adherence demands imposed by recent increases in product quality.

Processes using non-chromate coatings are taught in, for example, Japanese Laid Open (Kokai or Unexamined) Patent Application Numbers Sho 53-121034 (121,034/ 1978), Sho 57-44751 (44,751/1982), and Hei 1-177380 (177,380/1989). The art taught in Japanese Laid Open (Kokai or Unexamined) Patent Application Number Sho 53-121034 comprises a process for forming a coating on a metal surface by applying and drying thereon an aqueous solution containing water-dispersible silica, alkyd resin, and a trialkoxysilane compound. The coating afforded by this process, however, is unable to provide the level of corrosion resistance that is the object of this

invention. The art taught in Japanese Laid Open (Kokai or Unexamined) Patent Application Number Sho 57-44751 comprises a process that uses a water-soluble resin composed of a hydroxypyrone derivative, while the art taught in Japanese Laid Open (Kokai or Unexamined) Patent Application Number Hei 1-177380 comprises a process that uses a water-dispersible polymer of a hydroxystyrene compound or an aqueous solution of a hydroxystyrene compound. Again, neither of these processes can provide the level of corrosion resistance sought by this invention. Thus, the art as currently constituted is unable to provide a coating with a corrosion resistance high enough to permit use of the coating in place of a chromate film.

An object of this invention is to solve the problems described above for the prior art by providing a liquid surface treatment composition for application to metals that can form a highly corrosion-resistant, strongly paint-adherent coating on metal surfaces and particularly on the surface of zinciferous-plated steel sheet. An alternative and/or concurrent object of this invention is to provide a process for treating metal surfaces that uses this surface treatment composition.

BRIEF SUMMARY OF THE INVENTION

It has been found that a highly corrosion-resistant, strongly paint-adherent coating can be formed on metal surfaces by treating such surfaces with an aqueous liquid that, in addition to water, comprises, preferably consists essentially of, or more preferably consists of:

(A) a component of molecules that satisfy both of the following criteria:

(A.1) each molecule contains at least two moieties that conform to general formula (I):

$$\begin{array}{c} R^1O \\ | \\ R^2O\!-\!Si\!- \\ | \\ R^3O \end{array} \qquad (I),$$

wherein each of R^1, R^2, and R^3 is independently selected from the group consisting of hydrogen atoms and alkyl moieties containing from 1 to 4 carbon atoms; and

(A.2) for all of the molecules considered together, the weight average value for the molecular weight divided by the average number per molecule of moieties conforming to formula (I) as given above yields a quotient that is within a range from 100 to 30,000; and

(B) a component of one or more substances selected from the group consisting of organic acids, phosphoric acid, hydrofluoric acid, tetrafluoroboric acid,

hexafluorosilicic acid, hexafluorotitanic acid, hexafluorozirconic acid, hexafluorohafnic acid, and ammonium salts of organic acids, phosphoric acid, hydrofluoric acid, tetrafluoroboric acid, hexafluorosilicic acid, hexafluorotitanic acid, hexafluorozirconic acid, and hexafluorohafnic acid.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

In one preferred embodiment, a liquid treatment composition according to the invention also contains a component (C) selected from the group consisting of resins each of the molecules of which contains at least one tertiary amino moiety or quaternary ammonium moiety but does not qualify to be part of component (A). When component (C) is present, the weight of component (A) preferably has a ratio to the weight of component (C) in the same composition that is from 1.0:9 to 9:1.0, the weights of components (A) and (C) being measured in the same units.

In another preferred embodiment, a liquid treatment composition according to the invention also contains a component (D) selected from the water soluble salts of the metals cobalt, tungsten, vanadium, magnesium, aluminum, manganese, titanium, trivalent chromium, and molybdenum, exclusive of any such salts that could be part of any of components (A), (B), and (C) as described above but inclusive of salts in which the metals are part of oxycations as well as salts in which the metals are cations. When component (D) is present in a composition according to the invention, its weight preferably has a ratio to the weight of component (A) in the same composition that is from 0.00010:1.0 to 1.0:1.0, the weights of components (A) and (D) being measured in the same units.

In yet another preferred embodiment, a liquid treatment composition according to the invention also contains a component (E) selected from molecules each of which contains at least one moiety selected from the group consisting of C=O, C=C, C≡C, C=N, C≡N, N=N, N–N, and sulfur-atom-containing moieties, but exclusive of any molecules that could constitute part of any of components (A) through (D) as described above. When component (E) is present in a composition according to the invention, its weight preferably has a ratio the weight of component (A) in the same composition that is from 0.0010:1.0 to 1.0:1.0, the weights of components (A) and (E) being measured in the same units.

. A process according to this invention for treating metal surfaces is characterized by the formation of a liquid coating of a composition according to the invention on the surface of a metal substrate, and later, or preferably immediately, drying said surface treatment composition into place on said metal surface, without removing, e.g., by rinsing away, any of the non-volatiles content of the liquid coating before the coating is dried.

After drying, the coating film so formed should have a mass per unit area, often called "coating weight", that is from 0.1 to 3.0 grams of dried coating per square meter of metal surface coated, a unit of coating weight that is hereinafter usually abbreviated as "g/m^2".

Components (A) and (B) are the necessary active ingredients in a liquid surface treatment composition according to the invention. The weight average value for the molecular weight of component (A) divided by the average number per molecule of moieties conforming to formula (I) as given above in component (A) preferably has a value that is at least, with increasing preference in the order given, 120, 130, 140, 150, or 160 and independently preferably is not more than, with increasing preference in the order given, 10,000, 5000, 2000, 1500, 1000, or 800. Synthesis of a compound in which the molecular weight per functional group is below 100 is highly problematic. Adherence to the metal surface, which is a characteristic function of this functional group, declines when the value of the molecular weight per functional group exceeds 30,000. The nature of the parts of the molecules of component (A) that does not consist of moieties conforming to general formula (I) as described above is not critical, but these parts of the molecules of component (A) preferably are organic and more preferably contain, for example, ester, ether, acid amide, urethane, urea, or vinyl moieties.

While the process for synthesizing component (A) is not critical, this component can be synthesized, for example, by reacting chlorosilane with a compound bearing at least two active hydrogen-containing functional groups, by reacting two or more different silane coupling agents with each other, by reacting a reactive functional group-containing compound with the organofunctional groups in a silane coupling agent, and by copolymerizing a vinyl-functional silane coupling agent with other copolymerizable vinyl compound(s).

The use, as part of component (A), of molecules containing only one moiety conforming to general formula (I) in each molecule is undesirable because the presence of such molecules gives a diminished adherence to metal surfaces.

Organic acids, which are preferred over their salts, are advantageous constituents of component (B) as described above when treating zinc-coated steel, because organic acids do not strongly etch the zinc-coated steel sheet and nevertheless remove the very thin oxide film present on the surface of the plating. Strong acids such as sulfuric acid, hydrochloric acid, and nitric acid reduce the corrosion resistance because they remove too much of the zinc coating. The subject organic acid can be exemplified by formic acid, acetic acid, butyric acid, oxalic acid, succinic acid, lactic acid, L-ascorbic acid, tartaric acid, citric acid, DL-malic acid, malonic acid, maleic acid, and phthalic acid.

Phosphoric acid is believed to increase the corrosion resistance by forming a zinc phosphate conversion coating — albeit in very small amounts — on the surface of a zinciferous coating. Usable as this phosphoric acid are, for example, metaphosphoric acid, pyrophosphoric acid, orthophosphoric acid, triphosphoric acid, and tetraphosphoric acid and the ammonium, aluminum, and magnesium salts of these acids.

Fluoride when present as part of component (B) is believed to improve the corrosion resistance through a controlled etching activity and ability to chelate metal cations.

The various alternative types of substances suitable for component (B) have somewhat different preferred concentrations relative to component (A). In particular, for each 100 parts by weight of component (A) in a liquid composition according to the invention: when organic acids are used, their concentration preferably is at least, with increasing preference in the order given, 0.01, 0.05, 0.10, 0.50, 1.0, 3.0, or 4.0 and independently preferably is not more than, with increasing preference in the order given, 300, 200, 100, 75, 50, 25, 20, 10, or 6 parts by weight; when phosphoric acid is used, its concentration preferably is at least, with increasing preference in the order given, 0.05, 0.10, 0.50, 1.0, 3.0, or 4.0 and independently preferably is not more than, with increasing preference in the order given, 200, 100, 75, 50, 25, 20, 10, or 6 parts by weight; and when complex fluorides are used, their concentration preferably is at least 0.01, 0.05, 0.10, 0.50, 1.0, 3.0, 6.0, or 9.0 and independently preferably is not more than, with increasing preference in the order given, 100, 75, 50, 25, 20, 15, or 11 parts by weight. These preferences for the individual alternatives of component (B) apply even if more than one of them is used. Only a weak effect is generated by the addition of component (B) in an amount below these ranges. In contrast, no additional effect is obtained by an addition above the given ranges, and such additions are thus uneconomical.

The corrosion resistance afforded by this invention can be further improved by the addition of component (C), a resin whose molecules contain at least one tertiary amino moiety or quaternary ammonium moiety. While the type of resin is not critical, a general-purpose predominantly polyacrylic, epoxy, polyurethane, or polyester resin is preferred. The technique for introducing tertiary amino and/or quaternary ammonium moieties is also not critical. In this regard one can contemplate, for example, the use of an amino-functional comonomer during resin synthesis, the use of nitro- and/or nitrile-containing comonomers during resin synthesis followed by reduction of the nitro and/or nitrile moieties, and direct substitution of an amino moiety for C-bonded hydrogen in the resin. Any of these techniques is acceptable.

Component (C) when used preferably has a concentration that will result in a

ratio by weight of component (A) to component (C) that is at least, with increasing preference in the order given, 1.00:9.0, 1.00:7.0, 1.00:6.0, or 1.00:5.0 and independently preferably is not more than, with increasing preference in the order given, 9.0:1.00, 7.0:1.00, 6.0:1.00, or 5.0:1.00. The corrosion resistance is diminished when this ratio of (A)/(C) is below 1.0:9. Conversely, only a weak effect is generated by the addition of component (C) when (A)/(C) is above 9:1.0, making such a use of component (C) uneconomical.

The corrosion resistance afforded by this invention can also be further improved by the use of component (D). When used, component (D) preferably is present in an amount such that its ratio by weight to component (A) in the same treatment composition is at least, with increasing preference in the order given, 0.00010:1.0, 0.0005:1.00, 0.0010:1.00, 0.0050:1.00, 0.0100:1.00, 0.050:1.00, 0.070:1.00, 0.090:1.00, or 0.10:1.00 and independently preferably is not more than, with increasing preference in the order given, 1.00:1.00, 0.80:1.00, 0.70:1.00, 0.60:1.00, or 0.50:1.00. Little or no improvement in corrosion resistance is seen from a component (D) addition below 0.00010:1.0, while a component (D) addition above 1.0:1.0 is uneconomical since no additional benefit results from such an addition.

Further improvement in the corrosion resistance afforded by this invention can also be obtained by the addition of component (E), which is constituted of one or more substances that contain in each molecule at least one of the moieties represented by the following chemical formulas (with only essential bonds shown): C=O, C=C, C≡C, C=N, C≡N, N=N, N–N, and S. The thus functionalist compound is not particularly critical and can be exemplified by C=O-containing compounds such as aldehydes like formaldehyde and acetaldehyde and ketone like acetone and methyl ethyl ketone; by C=C-containing compounds such as benzene and derivatives thereof, naphthalene and derivatives thereof, (met)acrylic acid and derivatives thereof, the esters of alkenylcarboxylic acids, and alkenylaldehydes; by C≡C-containing compounds such as acetylene alcohol and acetylene derivatives; by C=N-containing compounds such as azine, triazine, osazone dyes, triphenylmethane dyes, guanidine, pyrimidine, pyrazole, imidazole, and pyridinium and quinolinium compounds; by C≡N-containing compounds such as ethylene cyanohydrin; by N–N-containing compounds such as hydrazine compounds and derivatives thereof; by N=N-containing compounds such as azo dyes; and by S-containing compounds such as sulfonic acid, sulfonates, sulfoamides, thiourea, and cyclic thiourea.

When component (E) is present, it preferably is present in an amount such that the ratio by weight of component (E) to component (A) in the same composition is at

least, with increasing preference in the order given, 0.0010:1.0, 0.0050:1.00, 0.010:1.00, 0.030:1.00, 0.050:1.00, 0.070:1.00, 0.080:1.00, 0.090:1.00, or 0.097:1.00 and independently preferably is not more than, with increasing preference in the order given, 1.00:1.00, 0.50:1.00, 0.40:1.00, 0.30:1.00, 0.20:1.00, or 0.12:1.00. Little or no improvement in corrosion resistance is obtained from a component (E) ratio below 0.0010:1.0, while the paint adherence is reduced when the (E)/(A) ratio is more than 1.0:1.0.

The surface treatment composition of this invention may also contain: additives such as thickeners and surfactants (the latter also known as wetting agents) for the purpose of generating a uniform coating on the substrate surface; electrical conductivity improvers in order to improve the welding behavior; colored pigments in order to improve the aesthetics, and film-forming auxiliaries in order to improve the film-forming performance.

The surface treatment composition of this invention is preferably applied, for example, to: aluminum sheet; steel sheet, e.g., cold-rolled steel sheet and hot-rolled steel sheet; and, most preferably, zinciferous-plated steel sheet, e.g., electrogalvanized steel sheet, hot-dipped galvanized steel sheet, galvannealed steel sheet, steel sheet plated with aluminum-containing zinc, Zn/Ni-plated steel sheet, Zn/Co-plated steel sheet, and vapor-deposition zinc-plated steel sheet.

A coating with a weight after drying of 0.1 to 3.0 g/m^2 is preferably formed by application of a surface treatment composition according to the invention to the metal surface by, for example, roll coating, dipping, or electrostatic coating, followed by drying by induction heating or with a hot gas current to an attained sheet temperature of 60 to 250 °C and preferably 80 to 220 °C. The performance of the resulting coating may often be unsatisfactory when the attained sheet temperature does not reach 60 °C, while an attained sheet temperature in excess of 250 °C can result in pyrolysis of the coating. The performance of the coating may often be unsatisfactory when the coating weight is less than 0.1 g/m^2, while no additional increments in coating performance are obtained at above 3.0 g/m^2, making such weights uneconomical.

The solids concentration in the surface treatment composition of the invention is preferably in the range from 1 to 50 %. Since the surface treatment composition is an aqueous system, a solids concentration below 1 % is undesirable because such concentrations result in long drying times. At the other end of the range, a solids concentration in excess of 50 % is undesirable because concentrations at this level cause such problems as a reduced dispersion stability and an increased viscosity of the treatment agent. Because a composition according to the invention is dried into place on the surface being treated in a process according to the invention, the concentration of the surface

treatment composition has little or no technical effect on the results obtained, provided that a preferred coating weight as described above is obtained. A preferred coating weight can be obtained with either a thick coating of a dilute surface treatment liquid or a thin coating of a concentrated surface treatment liquid.

This invention is illustrated in more specific terms in the following through working and comparative examples, but the scope of the invention is not limited by the working examples that follow. Described immediately below are the test specimens, degreasing treatment, and process for applying the metal surface treatment composition that were used in the working and comparative examples.

1. Preparation of the test specimens

(1-1) Materials tested

The following commercial materials were tested as substrates:

- electrogalvanized steel sheet (hereinafter usually abbreviated as "EG") sheet thickness = 0.8 millimeter (hereinafter usually abbreviated as "mm"), coating weight = 20 grams of electroplated zinc per square meter of steel sheet on both major surfaces, the unit of grams per square meter being hereinafter usually abbreviated as "g/m2" and coating on both major surfaces being hereinafter indicated by numbers with a virgule between them, so that the abbreviated description of this coating would be "20/20 g/m2";
- steel sheet hot-dip coated with zinc containing 5 % aluminum (hereinafter usually abbreviated as "GF")
  sheet thickness = 0.8 mm, coating weight = 90/90 g/m^2;
- Zn/Ni alloy-coated steel sheet (hereinafter usually abbreviated as "Zn/Ni")
  sheet thickness = 0.8 mm, coating weight = 20/20 g/m^2;
- hot-dip zinc-coated steel sheet (hereinafter usually abbreviated as "GI")
  sheet thickness = 0.8 mm, coating weight = 90/90 g/m^2;
- hot-dip 55 % Zn alloy-coated steel sheet (hereinafter usually abbreviated as "GL")
  sheet thickness = 0.8 mm, coating weight = 90/90 g/m^2;
- galvannealed (Zn-Fe) hot-dip zinc-coated steel sheet (hereinafter usually abbreviated as "GA")
  sheet thickness = 0.8 mm, coating weight = 60/60 (g/m^2); and
- A-1100 aluminum sheet (hereinafter usually abbreviated as "AL")
  sheet thickness = 0.8 mm.

(1-2) Degreasing treatment

The substrate was sprayed for 2 minutes at 60 °C with a solution in water of 20 grams, per liter of water, of FINECLEANER® 4336 concentrate for a silicate-type alkaline degreaser commercially available from Nihon Parkerizing Co., Ltd. This was followed by rinsing with pure water for 30 seconds and then drying.

(1-3) Application of the metal surface treatment composition

The metal surface treatment composition (see below for details) was applied with a bar coater. This was followed by drying at an ambient temperature of 300 °C.

2. Painted sheet performance testing

(2-1) Corrosion resistance in flat regions

Salt-spray testing as described in Japanese Industrial Standard (hereinafter usually abbreviated as "JIS") Z-2371 was carried out for 120 hours, after which the status of white rust development was evaluated and reported on the following scale:

+ + + = rust produced over less than 3 % of the total surface area;

+ + = rust produced over at least 3 % but less than 10 % of the total surface area;

+ = rust produced over at least 10 % but less than 30 % of the total surface area;

× = rust produced over at least 30 % of the total surface area.

(2-2) Corrosion resistance in worked regions

The Erichsen test (7 mm extrusion) was carried out as described in JIS Z-2247 followed by salt-spray testing according to JIS Z-2371 for 72 hours. The status of white rust development was then evaluated and reported on the following scale:

+ + + = rust produced over less than 10 % of the total surface area;

+ + = rust produced over at least 10 % but less than 20 % of the total surface area;

+ = rust produced over at least 20 % but less than 30 % of the total surface area;

× = rust produced over at least 30% of the total surface area.

(2-3) Overcoated paint adherence

The test specimen was coated with a melamine alkyd paint (Amilac™ #1000, registered trademark of Kansai Paint Co., Ltd.) in an amount sufficient to produce a 25 micrometre (hereinafter usually abbreviated as "μm") thick coating after baking. Coating was followed by baking for 20 minutes at 125 °C. Evaluation was run on painted test specimens after standing for 24 hours (primary test) and on test specimens that had been allowed to stand for 24 hours, then immersed in boiling water for 2 hours, and then allowed to stand for another 24 hours (secondary test). Evaluation consisted of scribing

a 100-square grid (1 mm interval), extruding the grid region 7 mm with an Erichsen tester, peeling with pressure-sensitive adhesive tape, and then scoring the extent of paint film peeling. The results were reported on the following scale:

+ + + : no. of peeled paint squares = 0;

+ + : no. of peeled paint squares = 1;

+ : no. of peeled paint squares = 2 to 10;

× : no. of peeled paint squares = 11 to 100.

3. **Metal surface treatment compositions**

TREATMENT COMPOSITION A

An amount of 5 parts by weight of ammonium dihydrogen phosphate as component (B) was added to 100 parts by weight of the compound afforded by the reaction in ethanol of 1.0 mole of hexamethylenediamine and 2.0 moles of γ-glycidoxypropyltrimethoxysilane as component (A). The resulting mixture was diluted with deionized water to give a solids concentration of 5 %. Component (A) in this instance had 2 moieties conforming to formula (I) per molecule, and its ratio of gram molecular weight to the number of such moieties per molecule was approximately 294.

TREATMENT COMPOSITION B

An amount of 5.0 parts by weight of oxalic acid as component (B) was added to 100 parts by weight of the compound(s) afforded by the reaction in N-methyl-2-pyrrolidone of 1.0 mole of bisphenol-A epoxy resin (EPON™ 828 type, hereinafter usually abbreviated as "#828 type") and 2.0 moles of γ-aminopropyltriethoxysilane as component (A). The resulting mixture was diluted with deionized water to give a solids concentration of 5 %. Component (A) in this instance had 2 moieties conforming to formula (I) per molecule, and its ratio of gram molecular weight to the number of such moieties per molecule was approximately 411.

TREATMENT COMPOSITION C

An amount of 10 parts by weight of ammonium fluorosilicate as component (B) was added to 100 parts by weight of the compound(s) afforded by emulsion polymerization in deionized water of 1.0 mole of acrylic acid, 5.0 moles of butyl acrylate, 5.0 moles of methyl methacrylate, and 3.0 moles of γ-methacryloxypropyltriethoxysilane as component (A). The resulting mixture was diluted with deionized water to give a solids concentration of 5 %. Component (A) in this instance had 3 moieties conforming to formula (I) per molecule, and its ratio of gram molecular weight to number of such moieties per molecule was approximately 694.

TREATMENT COMPOSITION D

To Treatment Composition A as described above was added 20 parts by weight,

per 100 parts by weight of component (A), of the polymer(s) afforded by the emulsion polymerization in deionized water of 1.0 mole of acrylic acid, 5.0 moles of methyl methacrylate, 3.0 moles of 2-hydroxyethyl methacrylate, and 2.0 moles of dimethylaminoethyl methacrylate as component (C). The resulting mixture was diluted with deionized water to give a solids concentration of 5 %. The component (A)/component (C) weight ratio was 5:1.0.

TREATMENT COMPOSITION E

An amount of 100 parts by weight, per 100 parts by weight of component (A), of compound(s) afforded by the reaction of 1.0 mole of #828 type epoxy resin and 2.0 moles of dimethyl ethanolamine followed by pH adjustment to 4.5 with acetic acid as component (C), was added to Treatment Composition B as described above. The resulting mixture was diluted with deionized water to a solids concentration of 5 %. The component (A)/component (C) weight ratio was 1.0:1.0.

TREATMENT COMPOSITION F

To Treatment Composition C as described above was added 500 parts (solids) by weight, per 100 parts by weight of component (A), of a water-based urethane resin containing tertiary amino and quaternary ammonium moieties (Adeka Bontiter™ HUX 670, registered trademark of Asahi Denka Kogyo Kabushiki Kaisha) as component (C). The resulting mixture was diluted with deionized water to a solids concentration of 5 %. The component (A)/component (C) weight ratio was 1.0:5.0.

TREATMENT COMPOSITION G

To Treatment Composition A as described above was added 10 parts by weight, per 100 parts by weight of component (A), of anhydrous magnesium acetate as component (D). The resulting mixture was diluted with deionized water to give a solids concentration of 5 %.

TREATMENT COMPOSITION H

To Treatment Composition B as described above was added 20 parts by weight, per 100 parts by weight of component (A), of ammonium metavanadate (NH_4VO_3) as component (D). The resulting mixture was diluted with deionized water to give a solids concentration of 5 %.

TREATMENT COMPOSITION I

To Treatment Composition C as described above was added 30 parts by weight, per 100 parts by weight of component (A), of aluminum phosphate ($AlPO_3$) as component (D). The resulting mixture was diluted with deionized water to give a solids concentration of 5%.

TREATMENT COMPOSITION J

To Treatment Composition A as described above was added 10 parts by weight, per 100 parts by weight of component (A), of 2-butyn-1,4-diol ($HOCH_2C{\equiv}CCH_2OH$) as component (E). The resulting mixture was diluted with deionized water to give a solids concentration of 5 %.

TREATMENT COMPOSITION K

To Treatment Composition B as described above was added 10 parts by weight, per 100 parts by weight of component (A), of thiourea (H_2NCSNH_2) as component (E). The resulting mixture was diluted with deionized water to give a solids concentration of 5 %.

TREATMENT COMPOSITION L

To Treatment Composition D as described above was added 20 parts by weight, per 100 parts by weight of component (A), of anhydrous magnesium acetate as component (D). The resulting mixture was diluted with deionized water to give a solids concentration of 5 %.

TREATMENT COMPOSITION M

To Treatment Composition E as described above was added 20 parts by weight, per 100 parts by weight of component (A), of ammonium metavanadate (NH_4VO_3) as part of component (D) and 30 parts by weight, per 100 parts by weight of component (A), of aluminum phosphate ($AlPO_3$) as the remaining part of component (D). The resulting mixture was diluted with deionized water to give a solids concentration of 5 %.

TREATMENT COMPOSITION N

To Treatment Composition F as described above was added 20 parts by weight, per 100 parts by weight of component (A), of anhydrous magnesium acetate as component (D) and 10 parts by weight, per 100 parts by weight of component (A), of thiourea (H_2NCSNH_2) as component (E). The resulting mixture was diluted with deionized water to give a solids concentration of 5 %.

TREATMENT COMPOSITION O

Amounts of 5 parts by weight, per 100 parts by weight of component (A), of ammonium dihydrogen phosphate as part of component (B) and 10 parts by weight, per 100 parts by weight of component (A), of ammonium fluorosilicate as the remainder of component (B) were added to 100 parts by weight of the compound(s) afforded by the reaction in ethanol of 1 mole hexamethylenediamine and 2 moles of γ-glycidoxypropyltrimethoxysilane as component (A). The resulting mixture was diluted with deionized water to give a solids concentration of 5 %. Component (A) in this instance had 2 moieties conforming to formula (I) per molecule, and its ratio of gram molecular weight to number of such moieties per molecule was approximately 294.

TREATMENT COMPOSITION P

Amounts of 5.0 parts by weight, per 100 parts by weight of component (A), of ammonium dihydrogen phosphate as part of component (B), 10.0 parts by weight, per 100 parts by weight of component (A), of ammonium fluorosilicate as the remainder of component (B), and 200 parts by weight(solids), per 100 parts by weight of component (A), of a water-based polyurethane resin containing tertiary amino and quaternary ammonium moieties (Adeka Bontiter™ HUX 760, registered trademark of Asahi Denka Kogyo Kabushiki Kaisha) as component (C) were added to 100 parts by weight of bis(trimethoxysilylpropyl)amine (A-1170 from Nippon Unicar Co., Ltd.) as component (A). The resulting mixture was diluted with deionized water to give a solids concentration of 5 %. Component (A) in this instance had 2 moieties conforming to formula (I) per molecule, and its ratio of gram molecular weight to number of such moieties per molecule was approximately 171. The ratio by weight of component (A) to component (C) was 1.0:2.0.

COMPARATIVE TREATMENT COMPOSITION Q

An amount of 10 parts by weight of ammonium fluosilicate, which in itself would be suitable to constitute component (B) of a composition according to this invention, was added to 100 parts by weight of the compound(s), with an average molecular weight of approximately 40,000, afforded by the emulsion polymerization in deionized water of 50 moles of acrylic acid, 100 moles of butyl acrylate, 100 moles of methyl methacrylate, 100 moles of 2-hydroxyethyl methacrylate, and 1.0 mole γ-methacryloxypropyltriethoxysilane as the closest to a proper component (A) as described above. This mixture was diluted with deionized water to give a solids concentration of 5 %. What might otherwise be component (A) in this instance had an average of only 1 moiety conforming to formula (I) per molecule, and its ratio of gram molecular weight to number of such moieties per molecule was approximately 40,000 — a value outside the range specified for component (A) according to the present invention.

COMPARATIVE TREATMENT COMPOSITION R

An amount of 1.0 part by weight of sulfuric acid was added to 100 parts by weight of the compound(s), corresponding to component (A) in a Treatment Composition according to this invention, afforded by the reaction in ethanol of 1.0 mole of hexamethylenediamine and 2.0 moles of γ-glycidoxypropyltrimethoxysilane. This mixture was then diluted with deionized water to give a solids concentration of 5 %. The compound(s) corresponding to component (A) in this instance had 2 moieties conforming to formula (I) per molecule, and their average ratio of gram molecular weight to number of such moieties per molecule was approximately 294. This Treatment Composition did not contain a compound qualifying as component (B), however, so that it was not

according to the invention.

COMPARATIVE TREATMENT COMPOSITION S

An amount of 5 parts by weight of phosphoric acid, a material suitable in itself to constitute component (B) of a treatment composition according to the invention, was added to 100 parts by weight of γ-mercaptopropyltrimethoxysilane (KBM803 from Shin-Etsu Chemical), a material that after suitable reaction might have constituted component (A) of a composition according to the invention. The resulting mixture was diluted with deionized water to give a solids concentration of 5 % by weight. The KBM803 material had only one moiety conforming to formula (I) per molecule, a value outside the inventive range.

COMPARATIVE TREATMENT COMPOSITION T

This treatment composition was produced by the suitable dilution of Zinchrom® 3360H chromate treatment agent, a product commercially available from Nihon Parkerizing Co., Ltd. and intended for imparting temporary corrosion resistance to zinc-coated steel sheet.

COMPARATIVE TREATMENT COMPOSITION U

This treatment composition was produced by the suitable dilution of Zinchrom® 3383 chromate treatment agent, a product commercially available from Nihon Parkerizing Co., Ltd. and intended for imparting intermediate corrosion resistance to zinc-coated steel sheet.

4. Test results

Table 1 reports the Example and Comparative Example numbers associated with the metal surface treatment compositions identified by letters above, while Table 2 reports the results of painted sheet performance testing using the metal surface treatment compositions. Numbers 1 through 25 in Table 2 refer to experiments in which coatings were formed by application of a metal surface treatment composition according to the invention. Good values were obtained in all performance categories (flat region corrosion resistance, worked region corrosion resistance, overcoated paint adherence) in all of these experiments. Numbers 27 to 31 in Table 2 refer to experiments that used the treatment agents of Comparative Examples 1 through 5 in Table 1 — treatment agents that fell outside the scope of the present invention. These latter experiments gave relatively poor results for at least one, and often all, of the flat region corrosion resistance, worked region corrosion resistance, and overcoated paint adherence.

Table 1

Test Identifier		Substrate	Treatment Composition Identifier	Peak Metal Temperature	Coating Weight, g/m^2
Working Examples	1	EG	A	100 °C	1.0
	2	EG	B	100 °C	1.0
	3	EG	C	100 °C	1.0
	4	EG	D	100 °C	1.0
	5	EG	E	100 °C	1.0
	6	EG	F	100 °C	1.0
	7	EG	G	100 °C	1.0
	8	EG	H	100 °C	1.0
	9	EG	I	100 °C	1.0
	10	EG	J	100 °C	1.0
	11	EG	K	100 °C	1.0
	12	EG	L	100 °C	1.0
	13	EG	M	100 °C	1.0
	14	EG	N	100 °C	1.0
	15	EG	O	100 °C	1.0
	16	EG	P	100 °C	1.0
	17	EG	A	80 °C	1.0
	18	EG	B	220 °C	1.0
	19	EG	C	100 °C	0.3
	20	EG	D	100 °C	3.0
	21	GF	E	100 °C	1.0
	22	GI	E	100 °C	1.0
	23	GA	E	100 °C	1.0
	24	GL	E	100 °C	1.0
	25	Zn-Ni	E	100 °C	1.0
	26	AL	E	100 °C	1.0
Comparative Examples	1	EG	Q	100 °C	1.0
	2	EG	R	100 °C	1.0
	3	EG	Q	150 °C	3.0
	4	EG	R	150 °C	3.0
	5	EG	S	100 °C	1.0
	6	GI	T	60 °C	15 mg of Cr/m^2
	7	EG	U	100 °C	40 mg of Cr/m^2

Table 2

Test Identifier from Table 1	Corrosion Resistance in:		Overcoated Paint Adherence	
	Flat Region	Worked Region	Primary	Secondary
Example 1	+ + +	+ +	+ + +	+ + +
Example 2	+ + +	+ +	+ + +	+ + +
Example 3	+ + +	+ +	+ + +	+ + +
Example 4	+ + +	+ + +	+ + +	+ + +
Example 5	+ + +	+ + +	+ + +	+ + +
Example 6	+ + +	+ + +	+ + +	+ + +
Example 7	+ + +	+ + +	+ + +	+ + +
Example 8	+ + +	+ + +	+ + +	+ + +
Example 9	+ + +	+ + +	+ + +	+ + +
Example 10	+ + +	+ + +	+ + +	+ + +
Example 11	+ + +	+ + +	+ + +	+ + +
Example 12	+ + +	+ + +	+ + +	+ + +
Example 13	+ + +	+ + +	+ + +	+ + +
Example 14	+ + +	+ + +	+ + +	+ + +
Example 15	+ + +	+ + +	+ + +	+ + +
Example 16	+ + +	+ +	+ + +	+ + +
Example 17	+ + +	+ +	+ + +	+ + +
Example 18	+ +	+ +	+ + +	+ + +
Example 19	+ + +	+ + +	+ + +	+ + +
Example 20	+ + +	+ + +	+ + +	+ + +
Example 21	+ + +	+ + +	+ + +	+ + +
Example 22	+ + +	+ + +	+ + +	+ + +
Example 23	+ + +	+ + +	+ + +	+ + +
Example 24	+ + +	+ + +	+ + +	+ + +
Example 25	+ + +	+ + +	+ + +	+ + +
Example 26	+ + +	+ + +	+ + +	+ + +
Comparative Example 1	×	×	+ +	+
Comparative Example 2	×	×	+ +	+
Comparative Example 3	+	+	+	+
Comparative Example 4	+	+	+	+
Comparative Example 5	×	×	+	+
Comparative Example 6	+	×	×	×
Comparative Example 7	+ +	+ + +	+ + +	×

CLAIMS

1. An aqueous liquid surface treatment composition for metals, said composition comprising water and the following components:

(A) a component of molecules that satisfy both of the following criteria:

(A.1) each molecule contains at least two moieties that conform to general formula (I):

$$\begin{array}{ccc} & R^1O & \\ & | & \\ R^2O - & Si & - \\ & | & \\ & R^3O & \end{array} \qquad (I),$$

wherein each of R^1, R^2, and R^3 is independently selected from the group consisting of hydrogen atoms and alkyl moieties containing from 1 to 4 carbon atoms; and

(A.2) for all of the molecules considered together, the weight average value for the molecular weight divided by the average number per molecule of moieties conforming to formula (I) as given above yields a quotient that is within a range from 100 to 30,000; and

(B) a component of one or more substances selected from the group consisting of organic acids, phosphoric acid, hydrofluoric acid, tetrafluoroboric acid, hexafluorosilicic acid, hexafluorotitanic acid, hexafluorozirconic acid, hexafluorohafnic acid, and ammonium salts of organic acids, phosphoric acid, hydrofluoric acid, tetrafluoroboric acid, hexafluorosilicic acid, hexafluorotitanic acid, hexafluorozirconic acid, and hexafluorohafnic acid.

2. A surface treatment composition according to claim 1, additionally comprising a component (C) selected from the group consisting of resins each of the molecules of which contains at least one tertiary amino moiety or quaternary ammonium moiety but does not qualify to be part of component (A).

3. A surface treatment composition according to claim 2, in which there is a ratio by weight of component (A) to component (C) that is from 1.0:9 to 9:10.

4. A surface treatment composition according to claim 3, additionally comprising a component (D) selected from the water soluble salts of the metals cobalt, tungsten, vanadium, magnesium, aluminum, manganese, titanium, trivalent chromium, and molybdenum, exclusive of any such salts that could be part of any of components (A), (B), and (C) as described above but inclusive of salts in which the metals are part of

oxycations as well as salts in which the metals are cations, said component (D) having a weight ratio to component (A) in said surface treatment composition that is from 0.00010:1.0 to 1.0:1.0.

5. A surface treatment composition according to claim 2, additionally comprising a component (D) selected from the water soluble salts of the metals cobalt, tungsten, vanadium, magnesium, aluminum, manganese, titanium, trivalent chromium, and molybdenum, exclusive of any such salts that could be part of any of components (A), (B), and (C) as described above but inclusive of salts in which the metals are part of oxycations as well as salts in which the metals are cations, said component (D) having a weight ratio to component (A) in said surface treatment composition that is from 0.00010:1.0 to 1.0:1.0.

6. A surface treatment composition according to claim 1, additionally comprising a component (D) selected from the water soluble salts of the metals cobalt, tungsten, vanadium, magnesium, aluminum, manganese, titanium, trivalent chromium, and molybdenum, exclusive of any such salts that could be part of any of components (A), (B), and (C) as described above but inclusive of salts in which the metals are part of oxycations as well as salts in which the metals are cations, said component (D) having a weight ratio to component (A) in said surface treatment composition that is from 0.00010:1.0 to 1.0:1.0.

7. A surface treatment composition according to claim 6, additionally comprising a component (E) selected from molecules each of which contains at least one moiety selected from the group consisting of C=O, C=C, C≡C, C=N, C≡N, N=N, N–N, and sulfur-atom-containing moieties, but exclusive of any molecules that could constitute part of any of components (A) through (D) as described above, said component (E) having a weight ratio to component (A) in said surface treatment composition that is from 0.0010:1.0 to 1.0:1.0.

8. A surface treatment composition according to claim 5, additionally comprising a component (E) selected from molecules each of which contains at least one moiety selected from the group consisting of C=O, C=C, C≡C, C=N, C≡N, N=N, N–N, and sulfur-atom-containing moieties, but exclusive of any molecules that could constitute part of any of components (A) through (D) as described above, said component (E) having a weight ratio to component (A) in said surface treatment composition that is from 0.0010:1.0 to 1.0:1.0.

9. A surface treatment composition according to claim 4, additionally comprising a component (E) selected from molecules each of which contains at least one moiety

selected from the group consisting of C=O, C=C, C≡C, C=N, C≡N, N=N, N–N, and sulfur-atom-containing moieties, but exclusive of any molecules that could constitute part of any of components (A) through (D) as described above, said component (E) having a weight ratio to component (A) in said surface treatment composition that is from 0.0010:1.0 to 1.0:1.0.

10. A surface treatment composition according to claim 3, additionally comprising a component (E) selected from molecules each of which contains at least one moiety selected from the group consisting of C=O, C=C, C≡C, C=N, C≡N, N=N, N–N, and sulfur-atom-containing moieties, but exclusive of any molecules that could constitute part of any of components (A) through (D) as described above, said component (E) having a weight ratio to component (A) in said surface treatment composition that is from 0.0010:1.0 to 1.0:1.0.

11. A surface treatment composition according to claim 2, additionally comprising a component (E) selected from molecules each of which contains at least one moiety selected from the group consisting of C=O, C=C, C≡C, C=N, C≡N, N=N, N–N, and sulfur-atom-containing moieties, but exclusive of any molecules that could constitute part of any of components (A) through (D) as described above, said component (E) having a weight ratio to component (A) in said surface treatment composition that is from 0.0010:1.0 to 1.0:1.0.

12. A surface treatment composition according to claim 1, additionally comprising a component (E) selected from molecules each of which contains at least one moiety selected from the group consisting of C=O, C=C, C≡C, C=N, C≡N, N=N, N–N, and sulfur-atom-containing moieties, but exclusive of any molecules that could constitute part of any of components (A) through (D) as described above, said component (E) having a weight ratio to component (A) in said surface treatment composition that is from 0.0010:1.0 to 1.0:1.0.

13. A process for treating metal surfaces, comprising an operation of forming a liquid coating with a non-volatiles content from 0.1 to 3.0 g/m^2 on the surface of a metal substrate by coating said substrate with a surface treatment composition according to any of claims 1 through 12 and then drying said surface treatment composition, without having removed from said liquid coating any of the non-volatiles content of said liquid coating.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/22363

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :C23C 22/05, 22/00; C09D 5/00, 183/00
US CL :106/14.11, 14.15, 14.41, 14.42, 14.43, 14.44; 148/251, 259, 260, 261, 262, 263, 267
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 106/14.11, 14.15, 14.41, 14.42, 14.43, 14.44; 148/251, 259, 260, 261, 262, 263, 267

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,846,342 A (AOYAMA et al) 08 December 1998, abstract, col. 2, line 39- - col. 3, line 35.	1-13
A	US 5,711,996 A (CLAFFEY) 27 January 1998.	1-13
A	US 5,750,197 A (VAN OOIJ et al) 12 May 1998.	1-13
A	US 5,868,820 A (CLAFFEY) 09 February 1999.	1-13
T	US 6,132,808 A (BROWN et al) 17 October 2000.	1-13

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
31 OCTOBER 2000

Date of mailing of the international search report
20 DEC 2000

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231
Facsimile No. (703) 305-3230

Authorized officer
ANTHONY J. GREEN
Jean Proctor
Paralegal Specialist
Telephone No. (703)-308-0661